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Reiner Memmer

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Computer Simulation of Chiral Liquid Crystal Phases

Reiner Memmer

Fachbereich Chemie
Universität Kaiserslautern, 67663 Kaiserslautern, Germany
E-mail: memmer@rhrk.uni-kl.de

Computer simulations, e.g. the Monte Carlo (MC) and molecular dynamics (MD) method, provide an important tool to aid the understanding of the macroscopic properties of condensed matter systems and of their phase transitions. In the field of liquid crystals, a state of matter with long range orientational order, many applications e.g. in display technology are due to material properties linked to the existence of helical superstructures originating from molecular chirality. Phase diagrams of chiral calamitic liquid crystals were investigated by MC in the canonical (NVT) and the isobaric-isothermal (NpT) ensemble in order to deduce a link between macroscopic and microscopic properties, e.g. the molecular structure, starting with interactions between the molecules. A rich polymorphism of chiral liquid crystal phases was observed in dependence on temperature, pressure and a chirality parameter. In addition to the cholesteric phase, for the first time several blue phases and a phase with characteristics of a twist grain boundary phase have been observed. Recently, the discovery of chiral superstructures in liquid crystal phases of achiral so-called banana-shaped molecules attracted considerable interest. On cooling an isotropic system of banana-shaped molecules, at low temperature a biaxial smectic phase with a local polar arrangement of the steric dipoles arranged in an antiferroelectric-like superstructure could be proven. Additionally, at intermediate temperature a nematic-like phase has been formed whereas hints for a spontaneous achiral symmetry breaking have been determined. The structures of all phases were characterised by order parameters, scalar and pseudoscalar orientational correlation functions, and by visual representations of selected configurations.

1 Introduction

Liquid crystal phases, formed by molecules with a characteristic shape anisotropy, are a state of matter with long range orientational order. Many of their applications e.g. in display technology¹ are due to material properties linked to the existence of helical superstructures originating from the chirality of mesogenic molecules which leads to a variety of chiral liquid crystal phases², see Fig. 1 for a typical phase diagram in the temperature-chirality parameter plane. Characteristic for these phases are helical superstructures in the arrangement of the molecules, i.e. the manifestation of suprastructural chirality, basing on a spontaneous twist of the molecular orientation. Well known examples for chiral liquid crystal phases without positional order are the cholesteric phase (N^*) and the blue phases (BP I, BP II, and BP III), which are formed by chiral calamitic and discotic molecules, in single component systems and induced by chiral dopants dissolved in achiral liquid crystal host phases. There exist also many chiral liquid crystal phases with positional order, where the formation of both a helical superstructure and a layered structure can be realised free of defects, as e.g. in smectic S_C^* phases of calamitic molecules or yields frustrated structures, as in the case of the recently discovered twist grain boundary phases (TGB) with a helical arrangement of smectic regions. In spite of the enormous success in the characterisation of new structures of chiral liquid crystal phases, relatively little is known about the connection between the molecular chirality and the suprastructural chirality of the phases, i.e. about

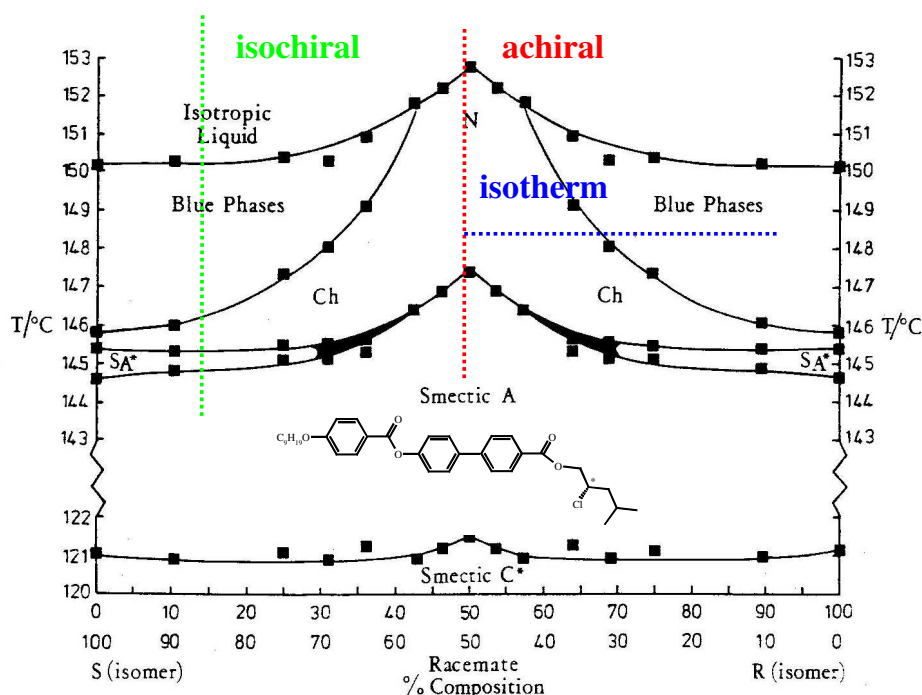


Figure 1. Miscibility phase diagram of binary mixtures of the enantiomers of a chiral compound (Fig. from³). Nematic and smectic phases are formed on cooling the racemate, cholesteric and blue phases appear along a selected isochiral in dependence on temperature as well as along an isotherm in dependence on composition.

the link between chirality at the microscopic and the macroscopic level, as recently pointed out by Lubensky et al.⁴ The determination of phase diagrams in the temperature-chirality parameter plane and of the phase structures has been subject of many experimental and theoretical investigations already since the discovery of liquid crystals, but in general it is very difficult to make predictions about the chiral liquid crystal phases or even the phase sequence appearing for a selected chiral mesogenic molecule. Recently, new types of liquid crystal phases formed by so-called banana-shaped molecules were discovered which show interesting material properties, e.g. the appearance of ferroelectricity^{5,6}. In these systems of achiral molecules the detected formation of chiral superstructures, i.e. a spontaneous achiral symmetry breaking, is even more remarkable and not yet fully understood. Here, many possible structures are still under discussion for the chiral domains.

Investigations by means of molecular modeling allow to deduce a link between microscopic and macroscopic properties starting with model interactions between the molecules and have been successfully applied in the field of liquid crystals⁷, but mainly restricted to achiral liquid crystals, e.g. nematic and smectic phases. Recently, a variety of model systems for cholesteric liquid crystal phases have been studied by means of computer simulation, e.g. systems of chiral atropisomeric molecules⁸ and lattice systems of chiral molecules⁹. In the following, computer simulation results will be presented for chiral calamitic molecules described by the chiral Gay-Berne fluid^{10,11}, the first model system

where a rich polymorphism of chiral liquid crystal phases could be proven in dependence on temperature, pressure and a chirality parameter. Additionally, a MC study of phase structures of systems composed of model Gay-Berne banana-shaped molecules will be presented¹².

2 Chiral Calamitic Molecules

In order to describe chiral calamitic molecules the chiral Gay-Berne fluid has been defined as an extension of the Gay-Berne fluid, a potential taking into account the molecular anisotropy in both the shape and the attractive forces which has been successfully used to describe achiral calamitic liquid crystals¹³. An additive chiral interaction term is taken into account in order to include the specific feature of chiral molecules, the energetic discrimination between mirror image arrangements. The total intermolecular interaction energy $U(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \mathbf{r}_{ij})$ between two chiral molecules i and j with orientations described by unit vectors $\hat{\mathbf{u}}_i$ and $\hat{\mathbf{u}}_j$ and separated by an intermolecular vector \mathbf{r}_{ij} is given by

$$U(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \mathbf{r}_{ij}) = aU_a(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \mathbf{r}_{ij}) + cU_c(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \mathbf{r}_{ij}), \quad (1)$$

where $U_a(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \mathbf{r}_{ij})$ denotes the energy of the achiral interaction taken to be the Gay-Berne potential¹³

$$U_a = 4\epsilon(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \mathbf{r}_{ij}) \left[\left(\frac{\sigma_0}{r_{ij} - \sigma(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \mathbf{r}_{ij}) + \sigma_0} \right)^{12} - \left(\frac{\sigma_0}{r_{ij} - \sigma(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \mathbf{r}_{ij}) + \sigma_0} \right)^6 \right]$$

and $U_c(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \mathbf{r}_{ij})$ is the energy of the chiral interaction given by

$$U_c = 4\epsilon(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \mathbf{r}_{ij}) \left(\frac{\sigma_0}{r_{ij} - \sigma(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \mathbf{r}_{ij}) + \sigma_0} \right)^7 \left[(\hat{\mathbf{u}}_i \times \hat{\mathbf{u}}_j) \cdot \mathbf{r}_{ij} \right] (\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j).$$

The strengths of the corresponding interaction energies are given in terms of dimensionless scalar and pseudoscalar parameters a and c , respectively, i.e. the latter one, the chirality parameter, changes sign if enantiomers are considered.

In order to investigate the influence of chirality on the structure of liquid crystal phases, the phase diagram in the temperature-chirality parameter plane of the chiral Gay-Berne fluid was studied as a function of the chirality parameter c along an isotherm in the stability range of the nematic phase (N) of the achiral Gay-Berne fluid. Systems of $N=2048$ molecules were investigated under periodic boundary conditions in a cubic box by MC in the canonical ensemble. Discontinuities of thermodynamic quantities, i.e. the energy and the second rank order parameter S^* , allowed the approximate localisation of appearing phase transitions and a first characterisation of the different phases. For low values of c the observed positive values of $S^* \approx 0.8$ indicate a favoured orientation of the long molecular axes $\hat{\mathbf{u}}_i$ parallel to a space-fixed axis, the director, a behaviour characteristic for nematic phases (Fig. 2a). The formation of nematic phases is maintained until a threshold value of c is reached. Then, values of $S^* \approx -0.4$ indicate a favoured orientation of the long molecular axes $\hat{\mathbf{u}}_i$ perpendicular to a selected space-fixed axis, i.e. a behaviour typical in a cholesteric phase with respect to the helical axis (Fig. 2b). Here, the continuous rotation of the favoured orientation of the long molecular axes along the helical axis is obvious. Finally, for higher values of c values of $S^* \approx 0.0$ are obtained, indicating an isotropic

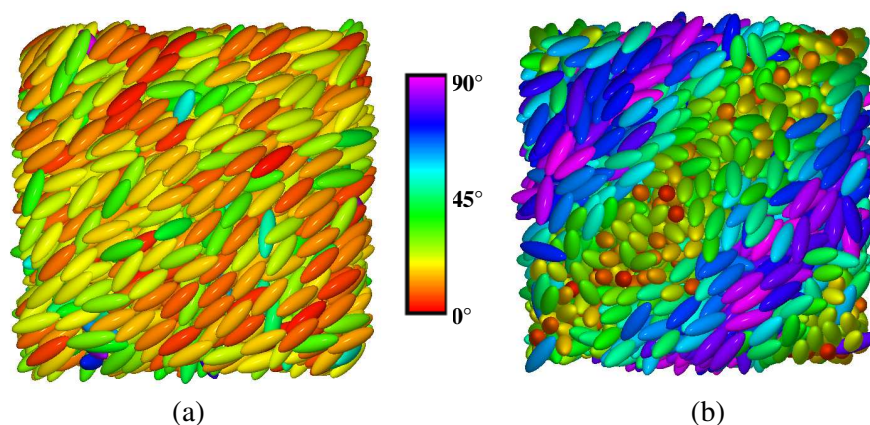


Figure 2. Visualisation of a configuration (MC- NVT) of (a) the nematic phase (N) and (b) the cholesteric phase (N^*) observed along an isotherm with increasing chirality parameter. For a schematic representation of its general shape each molecule is represented by an ellipsoid which is colour coded with respect to the angle between its long molecular axis and the director of the nematic phase and an axis perpendicular to the helical axis of the cholesteric phase.

character of the phase. Here, for many chiral mesogens often blue phases appear in the sequence BP I - BP II - BP III both with increasing temperature and chirality parameter (see Fig. 3a for a schematic phase diagram). The essential part in the theories of blue phases are so-called double twist cylinders characterised by a director field as sketched in Fig. 3b. Whereas in the cholesteric phase the twisting occurs only in one direction, i.e. along the helical axis, in a double twist cylinder a helical superstructure exists over a selected distance from the cylinder centre along every axis perpendicular to the cylinder axis. Different arrangements of such double twist cylinders taking into account unavoidable defects and isotropic regions have been considered in the framework of Landau-de Gennes theory. The network of interwoven double twist cylinders in a body-centred cubic structure, consistent with experimental results for BP I, is shown in Fig. 4a,b as elementary cell and in form of the resulting periodic structure. The corresponding characteristic features are obvious in the snapshot shown in Fig. 4c, where in spite of order parameters of zero regions with orientational correlations can be seen, especially if the angle between the long molecular axes and the box face normal is colour coded. There exist regions where the molecules are preferred parallel to the box face normal, whereas the preferred molecular orientation twists along all directions perpendicular to this axis moving away from these regions, i.e. helical superstructures appear but only locally and limited about a selected distance. The chiral Gay-Berne fluid is the first many particle system based on intermolecular interactions where such double twist structures, arranged here according to the structure of BP I, could be proved by computer simulation. At higher chirality parameter there still exist local double twist regions, but these are no longer infinite under the limitations of the system size nor arranged in a lattice. As in the so-called spaghetti model of blue phase III (Fig. 5a) the double twist regions are now worm-like and seem to be randomly oriented (Fig. 5b).

In general, the clear evidence should be emphasised that a chiral interaction potential proportional to the first pseudoscalar term of the expansion in rotational invariants is able

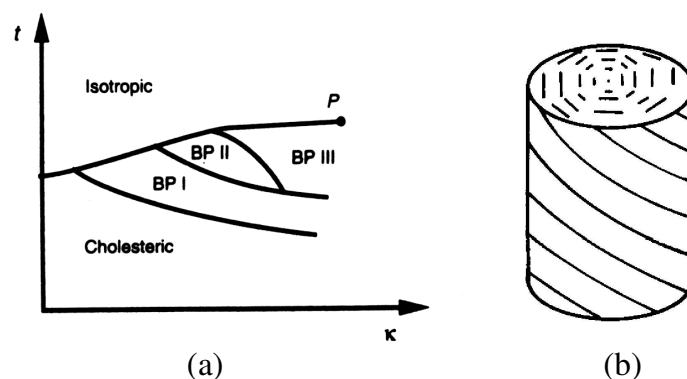


Figure 3. Blue phases: (a) Schematic phase diagram in the temperature-chirality parameter plane, (b) director field of a double twist cylinder.

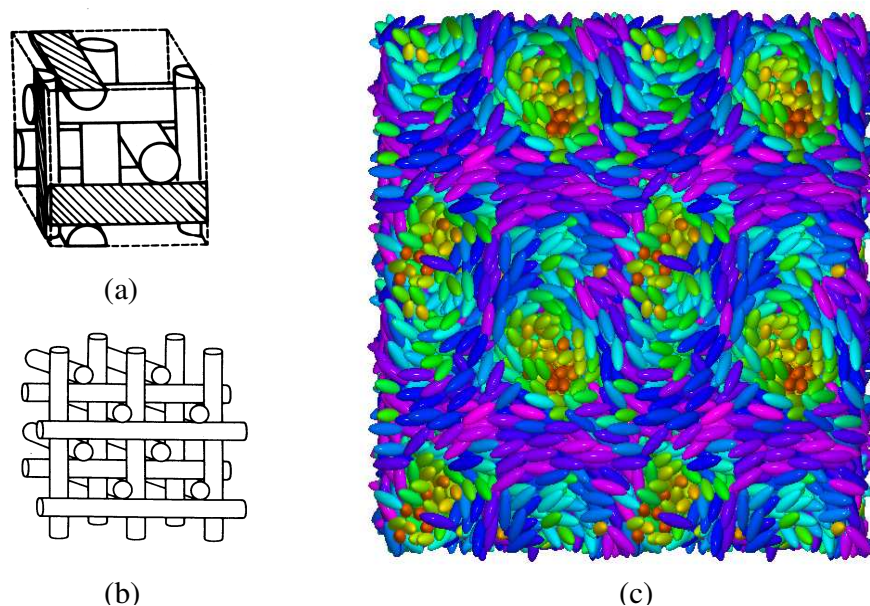


Figure 4. Blue phase I (BP I): Theoretical model, characterised by (a) arrangement of double twist cylinders in the unit cell, (b) three-dimensional arrangement, (c) visualisation of a configuration (MC-NVT) of BP I observed in dependence on chirality parameter along an isotherm.

to give the phase sequence nematic, cholesteric and blue phases as characteristic for many chiral mesogenic molecules in dependence on one pseudoscalar chirality parameter.

In canonical MC simulations of chiral liquid crystals generally cholesteric phases with non-equilibrium pitch were formed under periodic boundary conditions, which require that only selected orientations of the helical axis combined with an integral number of half turns of a cholesteric phase are possible in order to commensurate with the periodic images. In

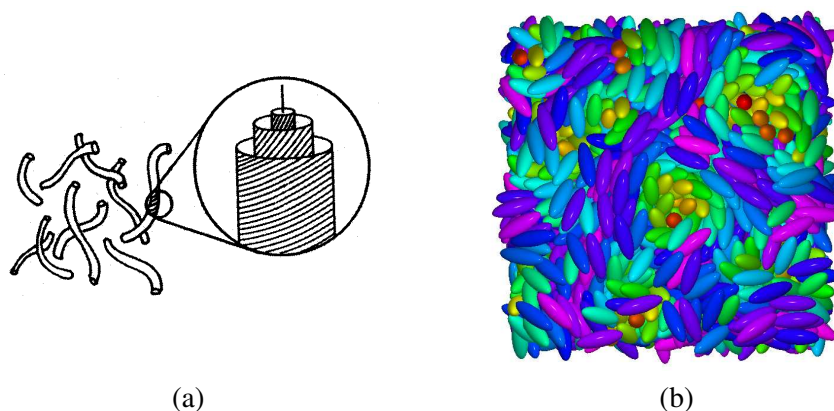


Figure 5. Blue phase III (BP III): (a) So-called spaghetti model with randomly oriented squirming double twist tubes, (b) visualisation of a configuration (MC- NVT) of BP III observed at high chirality parameter along an isotherm.

order to study the temperature influence on helical superstructures and to overcome system-size effects the phase diagram was additionally studied in the NpT ensemble. Here, the ability of the simulation box to change the dimensions during the simulation enabled the determination of the equilibrium pitch of cholesteric phases. Under isobaric conditions several phase transitions characterized by phase transition enthalpy, entropy and relative volume change have been identified in dependence on temperature along an isochiral. On heating a cholesteric phase, for the first time a temperature driven phase transition to a blue phase (BP II) could be proven by computer simulation, a characteristic feature of many experimental and theoretical phase diagrams of chiral liquid crystals. The network of interwoven double twist cylinders in a simple cubic structure, consistent with experimental results for BP II, is shown in Fig. 6a,b as elementary cell and in form of the resulting periodic structure. The corresponding characteristic features are obvious in the snapshot shown in Fig. 6c. Additionally, on cooling a cholesteric system a phase with a helical superstructure and smectic layers formed perpendicular to the helical axis has been observed. Shown in Fig. 7a-d are equidistant intersections chosen perpendicular to the helical axis. The molecular orientations are preferred perpendicular to the helical axis. Locally, the molecules have a favored orientation parallel to a common direction. In contrast to the absence of long-range positional order in a cholesteric phase, now additionally a layered structure has been formed along the local director with layer normals spiraling along the helical axis, one of the main characteristics of the molecular arrangement in a twist grain boundary (TGB) phase, shown for comparison in Fig. 7e.

The observed phase sequence TGB-like phase, cholesteric phase, blue phase and isotropic phase obtained in dependence on a scalar parameter, the temperature, corresponds well to the characteristics of many experimentally observed phase diagrams, e.g. the phase behavior of a binary non-racemic mixture of (S) and (R) enantiomers in dependence on temperature (Fig. 1).

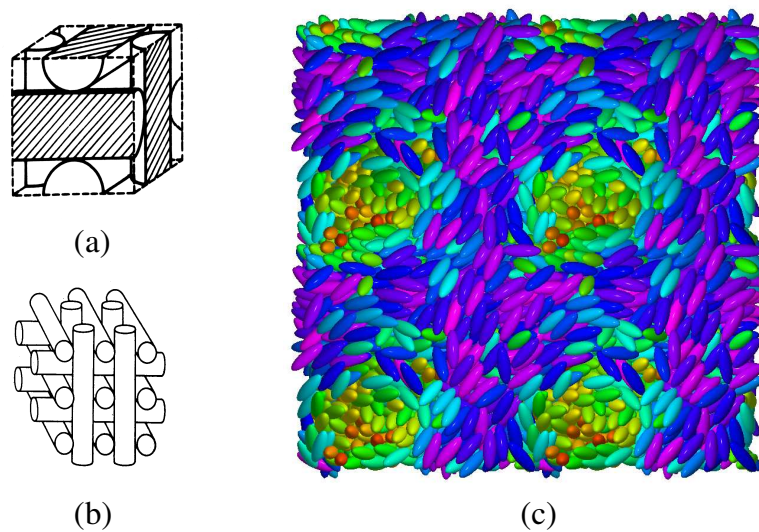


Figure 6. Blue phase II (BP II): Theoretical model, characterised by (a) arrangement of double twist cylinders in the unit cell, (b) three-dimensional arrangement, (c) visualisation of a configuration (MC- NpT) of BP II observed in dependence on temperature along an isochiral.

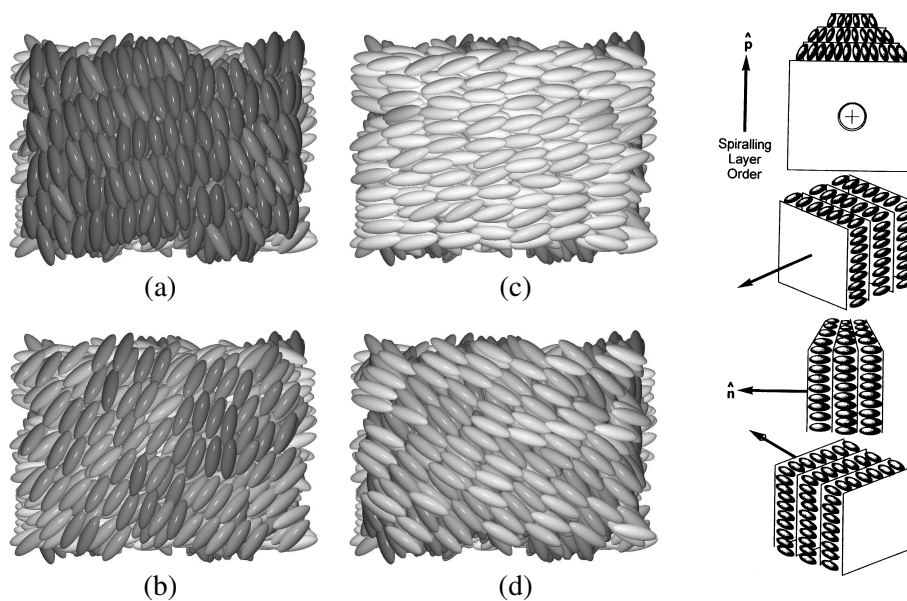


Figure 7. Characterization of a twist grain boundary phase (TGB): (a-d) Snapshot of the molecular organization in the TGB-like phase of the chiral Gay-Berne fluid visualized by equidistant intersections chosen perpendicular to the helical axis (MC- NpT); (e) molecular arrangement in a TGB A* phase (Fig. from¹⁴).

3 Achiral Banana-Shaped Molecules

The phase behaviour of achiral banana-shaped molecules described by model intermolecular interactions based on the Gay-Berne potential was studied by computer simulation. The characteristic molecular structure was considered by joining two calamitic Gay-Berne particles through a bond to form a biaxial molecule of point symmetry group C_{2v} (Fig. 8a) which has a steric dipole along the polar axis intersecting the bending angle. Systems of $N=1024$ rigid banana-shaped molecules with a bending angle of 140° have been studied in dependence on temperature by MC simulations in the NpT ensemble.

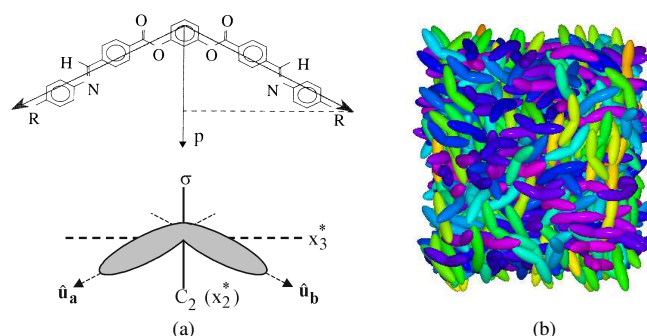


Figure 8. (a) Banana-shaped molecules: (above) chemical structure of a typical molecule, (below) a banana-shaped Gay-Berne molecule of point symmetry group C_{2v} with a steric dipole along the polar axis, defined by linking two equivalent calamitic Gay-Berne particles, (b) snapshot of the molecular organisation in the isotropic phase formed at high temperature.

On cooling down an isotropic system (Fig. 8b), two phase transitions characterised by transition enthalpy, entropy and relative volume change have been observed. For the first time, at low temperature an untilted smectic phase showing a global phase biaxiality and a spontaneous local polarisation in the layers, i.e. a local polar arrangement of the steric dipoles, with an antiferroelectric-like superstructure could be proven by computer simulation (Fig. 9b). The clear evidence should be emphasised that the spontaneous local polarisation and the antiparallel polarisation of neighbouring smectic layers are due to the anisotropy in shape and attractive interactions of the banana-shaped molecules with a steric dipole only without considering dipole-dipole interactions. Except the in-plane positional order the layered phase shows the characteristic structural features of the C_{PA} -phase, as recently observed experimentally for the first time for an achiral banana-shaped molecule having an achiral orthogonal biaxial smectic phase exhibiting antiferroelectric switching behaviour¹⁵. Additionally, at intermediate temperature a nematic-like phase has been proved (Fig. 9a), a feature which has been observed in systems of banana-shaped molecules only in exceptional cases. Here, close to the phase transition to the smectic phase hints for a spontaneous achiral symmetry breaking have been determined. A helical superstructure has been formed, with a structure (Fig. 9c) as recently predicted for achiral banana-shaped molecules considering the effects of a negative bend elastic constant with respect to the formation of nematic phases with spatially modulated director by means of a Landau-like model¹⁶.

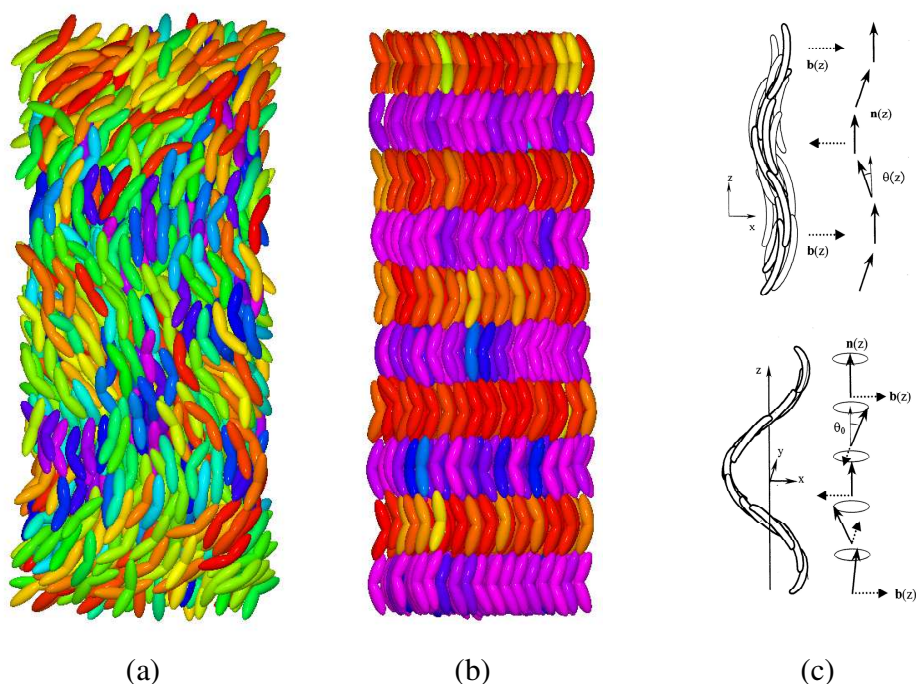


Figure 9. Snapshot of the molecular organisation (a) in the nematic phase and (b) in the biaxial smectic phase with a local polar arrangement of the steric dipoles arranged in an antiferroelectric-like superstructure, (c) theoretical model for nematic phases of banana-shaped molecules with spatially modulated director (Fig. from¹⁶).

4 Conclusions

Molecular systems of anisotropic molecules have been studied by computer simulation in order to figure out relationships between molecular structure and phase properties focussing especially to the formation of liquid crystal phases with suprastructural chirality. A rich polymorphism of liquid crystal phases was characterised in dependence on temperature, pressure, chirality parameter and molecular structure. A future task is now to extend the study to dynamical properties, especially taking into account the effects of external fields and surfaces.

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References

1. H. Coles, *Chiral nematics: Physical properties and applications*, in *Handbook of Liquid Crystals*, Vol. 2A, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill (Wiley-VCH, Weinheim, 1998), 335-409.
2. H.-S. Kitzerow, and C. Bahr (editors), *Chirality in liquid crystals* (Springer, New York, 2001).
3. A. J. Slaney, and J. W. Goodby, *The effect of molecular chirality on the incidence of twisted smectic A phases*, *Liq. Cryst.* **9**, 849-861 (1991).
4. T. C. Lubensky, A. B. Harris, R. D. Kamien, and G. Yan, *Chirality in liquid crystals: From microscopic origins to macroscopic structure*, *Ferroelectrics* **212**, 1-20 (1998).
5. D. R. Link, G. Natale, R. Shao, J. E. MacLennan, N. A. Clark, E. Körblova, and D. M. Walba, *Spontaneous formation of macroscopic chiral domains in a fluid smectic phase of achiral molecules*, *Science* **278**, 1924-1927 (1997).
6. T. Lubensky, *New banana phases*, *Science* **288**, 2146-2147 (2000).
7. P. Pasini, and C. Zannoni (editors), *Advances in the computer simulations of liquid crystals* (Kluwer Academic Publishers, Dordrecht, 1999).
8. R. Memmer, H.-G. Kuball, and A. Schönhofer, *Computer simulation of chiral liquid crystal phases, III. A cholesteric phase formed by chiral Gay-Berne atropisomers*, *Mol. Phys.* **89**, 1633-1649 (1996).
9. R. Memmer, and F. Janssen, *Computer simulation of chiral liquid crystal phases, IX. Chiral induction in guest-host systems - calculation of the helical twisting power*, *Z. Naturforsch.* **54a**, 747-754 (2000).
10. R. Memmer, *Computer simulation of chiral liquid crystal phases, VIII. Blue phases of the chiral Gay-Berne fluid*, *Liq. Cryst.* **27**, 533-546 (2000).
11. R. Memmer, *Determination of equilibrium pitch of cholesteric phases by isobaric-isothermal Monte Carlo simulation*, *J. Chem. Phys.* **114**, 8210-8222 (2001).
12. R. Memmer, *Liquid crystal phases of achiral banana-shaped molecules - A computer simulation study*, *Liq. Cryst.* (2001) in press.
13. M. A. Bates, and G. R. Luckhurst, *Computer simulation of liquid crystal phases formed by Gay-Berne mesogens*, in *Liquid Crystals I*, edited by D. M. P. Mingos (Springer, Berlin, 1999), 65-137.
14. J. W. Goodby, *Twist grain boundary (TGB) phases*, in *Liquid Crystals II*, edited by D. M. P. Mingos (Springer, Berlin, 1999), 83-147.
15. A. Eremin, S. Diele, G. Pelzl, H. Nadasi, W. Weissflog, J. Salfetnikova, and H. Kresse, *Experimental evidence for a C_{PA}-phase: An orthogonal biaxial smectic phase without in-plane order exhibiting antiferroelectric switching behaviour*, 6th European Conference on Liquid Crystals, 25-30 March 2001, Halle, Germany.
16. I. Dozov, *Symmetry breaking in achiral banana-shaped nematics?*, 6th European Conference on Liquid Crystals, 25-30 March 2001, Halle, Germany.